

# **Synthesis of block copolymers with poly(methyl methacrylate): P(B-b-MMA), P(EB-b-MMA), P(S-b-B-b-MMA) and P(S-b-EB-b-MMA)**

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## Summary

Well-defined diblock copolymers poly(butadiene-b-methyl methacrylate) (= P(B-b-MMA)) and triblock copolymers poly(styrene-b-butadiene-b-methyl methacrylate) (= P(S-b-B-b-MMA)) have been prepared by sequential anionic polymerization in THF. The synthesis of P(B-b-MMA) and P(S-b-B-b-MMA) was most efficient in the presence of lithium alkoxides. By this method side reactions are suppressed and the polymerization can be performed at higher temperatures. The resulting triblock copolymers have narrow molecular weight distribution. The 1,2-PB midblock was quantitatively hydrogenated with tosylhydrazide to enhance thermal stability. Alternatively the hydrogenation can be performed at elevated pressure using hydrogen and Wilkinson-catalyst in butanone. Heterogeneous catalyst systems based on Palladium did not yield quantitative hydrogenation.

## Introduction

Recently, much attention has focused on block copolymers which contain a PMMA block in the field of block copolymer compatibilizers for polymer blends (1-4). PMMA is compatibel with several important polymers like PSAN (= Poly(styrene-co-acrylonitrile), PVC (= Polyvinylchloride) or PVF<sub>2</sub> (= Polyvinylidenfluoride). In the course of our work on polymer blends, we investigated in detail the compatibilizing capabilities of P(S-b-MMA) block copolymers for blends of PSAN and PPE (= Poly-2,6-dimethyl-1,4-phenylene ether) (5,6). This represents an amorphous blend system of the type A/C-D/B, in which the blocks of the compatibilizer are chemically different from, but thermodynamically miscible with the blend components. We extended this work to systems, in which we use poly(styrene-b-ethylene-co-1-butene-b-methyl methacrylate) triblock copolymers (= P(S-b-EB-b-MMA)) as compatibilizers (7). Here we report the synthesis and characterization of these block copolymers by sequential anionic polymerization in the presence of lithium alkoxides and the quantitative hydrogenation under conditions which preserve the narrow molecular weight distribution.

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## Experimental

### Anionic Polymerization

**Materials:** All monomers and 1,1-diphenylethylene were reagent grade materials. Di-n-butylmagnesium ( $\text{MgBu}_2$ ) was used as 0.5M solution in heptane, ( $\text{AlEt}_3$ ) as 1M solution in hexane. THF was technical grade and purified first by distillation under nitrogen from  $\text{CaH}_2$  and then refluxing over potassium. Styrene was predried with  $\text{CaH}_2$  and condensed from  $\text{MgBu}_2$  under high vacuum into teflon stoppered ampoules. Butadiene was condensed onto  $\text{MgBu}_2$ , stirred for several hours and then directly condensed into the reactor. MMA was predried with  $\text{CaH}_2$ , carefully degassed by freeze-thaw cycles in high vacuum, mixed with  $\text{AlEt}_3$ -solution until a yellow colour persisted and then condensed into ampoules (8). The glass ampoules with the purified liquid monomers were stored at liquid nitrogen temperature until use. 1,1-Diphenylethylene was purified by distillation from the deep red initiator solution with n-BuLi under nitrogen and handled with syringes.

**Equipment:** The basic equipment consists of a 1.6l stirred glass reactor with a thermostated cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Nitrogen was purified with Hydrosorb- and Oxsorb-columns (Messer Griesheim). Monomers were introduced from glass ampoules via a spherical joint. Initiator and capping agents were handled with syringes.

**P(S-b-B-b-MMA):** In a typical procedure 20ml n-BuLi (1.4M in hexane) were added to 1200ml purified THF and aged at room temperature over night. On the next day, styrene was introduced and cooled to  $-80^\circ\text{C}$ . The polymerization was initiated with n-BuLi under vigorous stirring to give the orange solution of living PS. After 30min butadiene was condensed into the reactor and the colourless solution warmed up to  $-10^\circ\text{C}$ . Depending on the molecular weight of the midblock, butadiene was polymerized during 4-6h. Under these conditions most of the butadiene ( $> 90\%$ ) had reacted. After this time an excess of 1,1-diphenylethylene was added to the solution. The red colour gradually developed within minutes. After cooling down to  $-60^\circ\text{C}$ , MMA was slowly added. The colourless solution was warmed to  $-40^\circ\text{C}$  and stirred for 1h to complete the reaction. The triblock copolymer was terminated and isolated by precipitation into MeOH. During the synthesis, aliquots of the PS block and the end-capped P(S-b-B) intermediate were isolated for analytical purposes. About 80g of polymer were produced by this technique.

**P(B-b-MMA):** The reaction conditions were the same as in the case of P(S-b-B-b-MMA). Butadiene was condensed to a solution of the initiator n-BuLi in THF with lithium alkoxides at  $-40^\circ\text{C}$ . After the polymerization of butadiene at  $-10^\circ\text{C}$ , the PB block was capped with 1,1-diphenylethylene. MMA was added at  $-60^\circ\text{C}$  and polymerized at  $-40^\circ\text{C}$  for 1h.

### Hydrogenations

**Hydrogenation with Diimine:** Reagent grade tosylhydrazide was used without purification. Technical grade toluene was purified by distillation from sodium under nitrogen. In a typical procedure 500ml toluene were first refluxed under a slow stream

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of nitrogen to remove traces of oxygen. After complete dissolution of 5g of polymer and  $\approx 50\text{mg}$  stabilizing agent (2,6-di-t-butyl-4-methylphenol), a 4-fold excess (relative to double bonds) of tosylhydrazide was added and kept 4-5h to reflux. The byproduct from the thermal decomposition of tosylhydrazide, p-toluenesulphonic acid precipitates from the solution. After dilution with 500ml toluene, the sulphonic acid is filtered off, the solution concentrated and the hydrogenated polymer isolated by precipitation into excess methanol. Further purification from p-toluenesulphonic acid was performed by precipitation of THF-solutions of the polymers into methanol.

Hydrogenation with homogeneous catalyst: The basic equipment was a 300ml laboratory autoclave with magnetic stirring device. 1g block copolymer with 50 mg stabilizing agent (2,6-di-t-butyl-4-methylphenol) were dissolved in 100-120ml butanone (reagent grade). After adding the Wilkinson-catalyst tris(triphenylphosphine)-rhodium(I)chloride (0.8 Mol% relative to double bonds), the hydrogenation was performed at 90bar  $\text{H}_2$ -pressure at  $50^\circ\text{C}$  for at least 24h. The hydrogenation is quantitative without broadening of the molecular weight distribution. No attempts have been made to determine the minimum amount of catalyst and the minimum time for complete hydrogenation. The hydrogenated block copolymer was isolated by precipitation into methanol. Complete removal of residual catalyst was achieved by filtration of a 1% w/v THF solution of the block copolymer through a short column (1cm) of basic  $\text{Al}_2\text{O}_3$ .

#### Analysis

Gel permeation chromatography (GPC) was performed in THF with a set of  $10\mu\text{m}$  PL-Gel-columns ( $10^5$ ,  $10^4$ ,  $10^3$  and  $10^2$  Å) with refractive index and UV detection at 254nm. Calibration with PS-standards. Membrane osmometry: Hewlett Packard high speed osmometer 502, the solvents were toluene,  $\text{CHCl}_3$  or THF.  $^1\text{H-NMR}$ : 200MHz,  $\text{CDCl}_3$

#### Results and discussion

##### Synthesis of P(S-b-B-b-MMA)

It is well-known that defined P(S-b-MMA) diblock copolymers can be prepared by sequential anionic polymerization of styrene and MMA (9). The reaction is best performed in polar solvents like THF at low temperatures. Under these conditions the polymerization of MMA is living and essentially free from side reactions. After polymerization of styrene at low temperatures, the living ends have to be capped with a suitable capping agent like 1,1-diphenylethylene in order to reduce the nucleophilicity. Otherwise there will be significant termination by attack to the carbonyl groups of MMA in the crossover step (10). Therefore the synthesis of P(S-b-B-b-MMA) by sequential anionic polymerization should also be best performed in THF with capping of the PB block.

The synthesis of P(B-b-MMA) diblock copolymers with 1,4-PB block is described in literature (11,12). After the polymerization of the PB block in apolar solvent like cyclohexane or benzene, THF was added as cosolvent. In contrast to this, we performed the whole synthesis of P(S-b-B-b-MMA) in THF according to the scheme in Figure 1. Under these conditions predominantly 1,2-microstructure of the butadiene block results.

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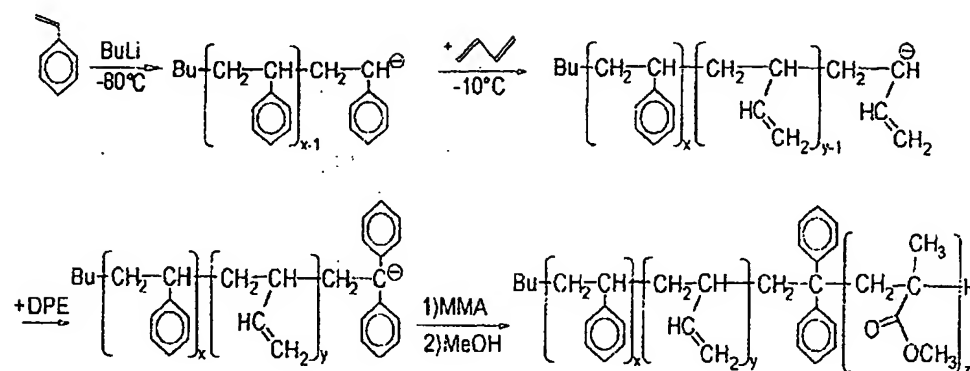


Figure1: Reaction scheme for the synthesis of P(S-b-B-b-MMA) by sequential anionic polymerization; DPE = 1,1-diphenylethylene

A problem arises due to the low stability of living PB in THF. Under the same reaction conditions, living PB is much less stable in THF than living PS (13). Nevertheless the rate of polymerization of butadiene is smaller than of styrene. Such behavior causes problems with respect to the preparation of block copolymers because longer reaction times favour termination.

In the first efforts to synthesize P(S-b-B-b-MMA) in pure THF, butadiene was polymerized at low temperatures between  $-40^\circ\text{C}$  and  $-75^\circ\text{C}$ . In each case significant amounts of the block copolymers were terminated during or after the polymerization of butadiene. For the preparation of defined P(S-b-B-b-MMA) without termination of the P(S-b-B) intermediate, it was therefore necessary to optimize the reaction conditions during the polymerization of butadiene.

Sigwalt et. al found that temperatures below  $-40^\circ\text{C}$  are necessary for the preparation of block copolymers with PB in THF (14). Bywater et. al showed that strong dissociated inorganic salts like lithiumtetraphenylborate enhance the stability of the carbanionic PB ends (13). In this case the polymerization is living up to higher temperatures. Recently much attention has focused on the stabilizing effects of salts like LiCl on the anionic polymerization of methacrylates and acrylates, which can therefore be polymerized in living fashion at much higher temperatures (15,16). Similar stabilizing effects on the polymerization of methacrylates, styrenes and conjugated dienes are also reported from alkoxides (10,17,18).

On the basis of the beneficial effects of alkoxides, we developed a simple procedure to synthesize well-defined P(S-b-B-b-MMA) triblock copolymers in the presence of lithium alkoxides. Organolithium compounds are not stable at room temperature in THF due to the attack on the  $\alpha\text{-CH}_2$  group. By the pathways outlined in Figure 2, alkoxides and enolates are formed by the reaction of organolithium compounds with the solvent (19). We used the reaction of  $n\text{-BuLi}$  with THF at room temperature to introduce lithium alkoxides into the reaction medium. This is simply accomplished by aging a mixture of THF and  $n\text{-BuLi}$  at room temperature over night. The concentration was about  $0.025\text{Mol Li}^+$  per 1l THF.

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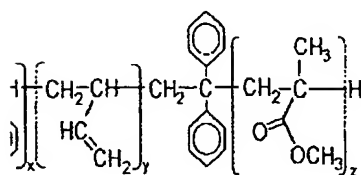
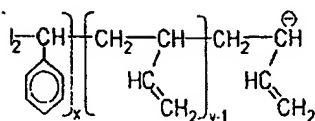
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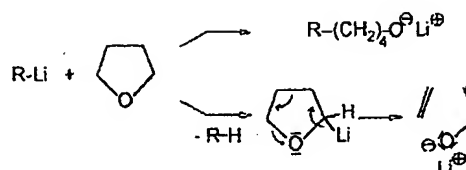


Figure 2: Possible reaction pathways of organolithium compounds with THF (19).

Under the reaction conditions we used, the reaction products of n-BuLi with THF showed no initiating capability for the monomers. Also no reaction with the ester carbonyl groups of the PMMA block could be detected. Besides the convenience of this procedure, it has also the advantage that traces of impurities in the reactor and the solvent are eliminated by reaction with n-BuLi. In comparison to the LiCl-method it is also not necessary to dry the salt by special procedures.

In the presence of lithium alkoxides, the polymerization rates were strongly reduced. Especially the polymerization of butadiene and MMA took much longer. Due to the stabilizing effect of lithium alkoxides, butadiene could be polymerized at higher temperatures between -5°C and -15°C without termination. After capping of the PB block with 1,1-diphenylethylene, MMA was polymerized at -40°C. Under these conditions well-defined P(S-b-B-b-MMA) triblock copolymers were synthesized without significant amounts of terminated PS-homopolymer or P(S-b-B) intermediate. Under the same reaction conditions defined P(B-b-MMA) diblock copolymers with 1,2-PB block were prepared too.

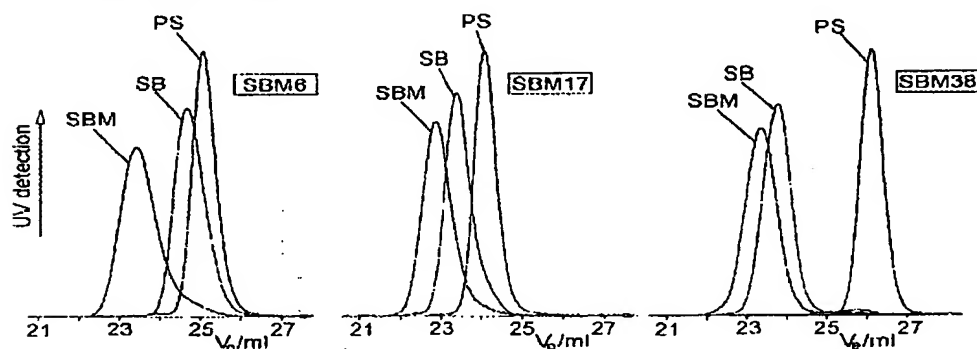


Figure 3: GPC analysis of P(S-b-B-b-MMA) triblock copolymers and the corresponding precursors; peaks are normalized to same area.

Figure 3 shows the GPC analysis of different P(S-b-B-b-MMA) triblock copolymers together with the corresponding PS and P(S-b-B) precursors. Table 1 gives the analytical results of these block copolymers. The molecular weight of the PS precursor can be accurately determined by GPC and membrane osmometry. Due to the PS calibration the molecular weight (from GPC) of the P(S-b-B) intermediate and the triblock copolymers are too low. The most reliable molecular weights of the triblock copolymers can be calculated from the molecular weight of the PS block and the chemical composition determined from <sup>1</sup>H-NMR. These calculated molecular weights

were in agreement with the results from membrane osmometry. According  $^1\text{H-NMR}$  the PB midblock contains 90 Mol% 1,2-units.

Table 1: Analytical results of P(S-b-B-b-MMA) triblock copolymers

	PS		P(S-b-B)		P(S-b-B-b-MMA)				
	$M_n$	$M_w/M_n$	$M_n$	$M_w/M_n$	$M_n$	$M_w/M_n$	$w_{PS}$	$w_{PB}$	$w_{PMMA}$
SBM6									
GPC:	80	1.04	(93)	1.06	(165)	1.11	0.45	0.06	0.49
Osmometry:	88		96		225				
SBM17									
GPC:	100	1.05	(148)	1.06	(205)	1.10	0.48	0.17	0.35
Osmometry:	108		145		238				
SBM38									
GPC:	57	1.04	(135)	1.07	(189)	1.08	0.24	0.38	0.38
Osmometry:	64		175		245				

The number after SBM denotes the weight fraction of the elastomeric midblock; molecular weights in kg/Mol; in brackets: GPC molecular weights of the P(S-b-B) intermediate and the triblock copolymer are too low due to PS-calibration;  $w_{PS}$ ,  $w_{PB}$ ,  $w_{PMMA}$  = weight fraction of the components determined from  $^1\text{H-NMR}$

#### Hydrogenation of P(S-b-B-b-MMA) with tosylhydrazide

The quantitative hydrogenation of P(S-b-B-b-MMA) was performed according the method of Lenz et. al with tosylhydrazide in refluxing toluene (21). The resulting P(S-b-EB-b-MMA) triblock copolymers preserved the narrow molecular weight distribution. Fig.4 shows the GPC traces of the hydrogenated triblock copolymers in comparison with the unsaturated triblock copolymers.

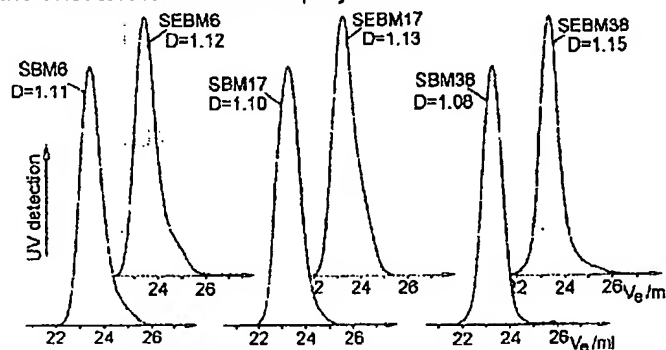


Figure 4: GPC analysis of P(S-b-EB-b-MMA) triblock copolymers (= SEBM) in comparison with the corresponding P(S-b-B-b-MMA) (= SBM);  $D = M_w/M_n$

Small amounts of p-toluenesulphonic acid are incorporated into the elastomer midblock by electrophilic addition to the double bonds. From  $^1\text{H-NMR}$ , the fraction of incorporated tosyl groups is estimated to be about 3 Mol% relative to double bonds in accordance with literature data (21). Figure 5 shows the  $^1\text{H-NMR}$  spectra of the P(S-b-EB-b-MMA) triblock copolymer SEBM38 hydrogenated with tosylhydrazide.

osmometry. According  $^1\text{H-NMR}$

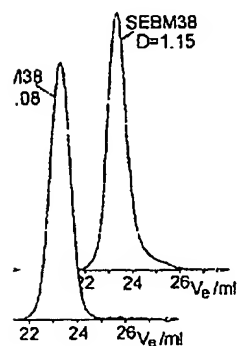
### block copolymers

P(S-b-B-b-MMA)			
$M_w/M_n$	$w_{PS}$	$w_{PB}$	$w_{PMMA}$
1.11	0.45	0.06	0.49
1.10	0.48	0.17	0.35
1.08	0.24	0.38	0.38

in of the elastomeric midblock;  
molecular weights of the P(S-b-B)  
due to PS-calibration;  $w_{PS}$ ,  $w_{PB}$ ,  
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MMA) (= SBM);  $D = M_w/M_n$   
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s. From  $^1\text{H-NMR}$ , the fraction of  
3 Mol% relative to double bonds  
shows the  $^1\text{H-NMR}$  spectra of the  
hydrogenated with tosylhydrazide.

According to a quantitative hydrogenation, the absorptions between 4.8 and 5.7 ppm completely disappeared.

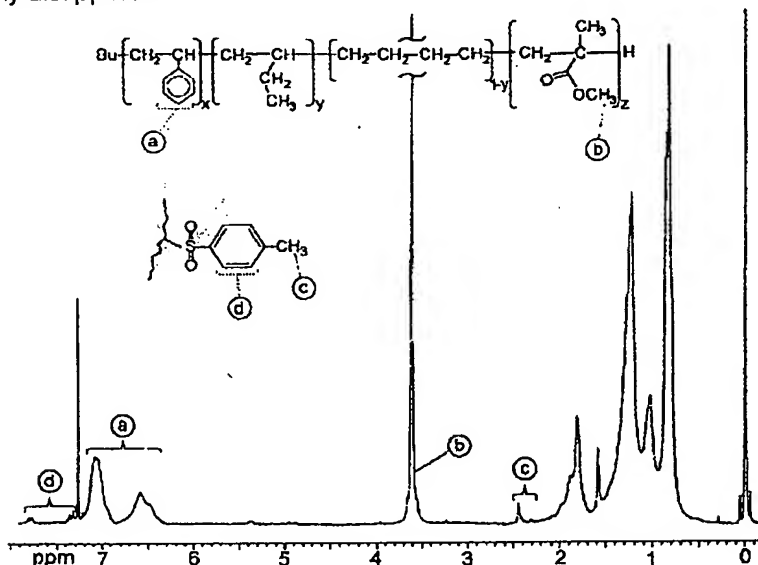


Figure 5:  $^1\text{H-NMR}$  analysis of the P(S-b-EB-b-MMA) triblock copolymer SEBM38 hydrogenated with tosylhydrazide.

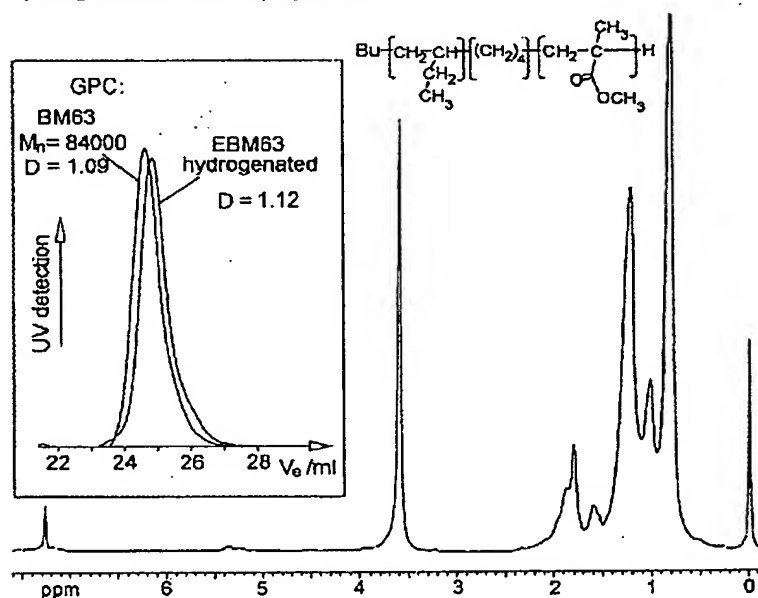


Figure 6:  $^1\text{H-NMR}$  analysis of the P(EB-b-MMA) diblock copolymer EBM63 hydrogenated with Wilkinson-catalyst. Insert: GPC analysis of the unsaturated and the hydrogenated diblock copolymer.

Alternatively P(S-b-B-b-MMA) triblock copolymers and P(B-b-MMA) diblock copolymers can also be quantitatively hydrogenated with hydrogen and Wilkinson-catalyst in butanone (22). Representatively, Figure 6 shows the  $^1\text{H-NMR}$  and GPC analysis of the hydrogenation of the P(B-b-MMA) diblock copolymer BM63 (63 wt% of PB). Under mild reaction conditions ( $\text{H}_2$ -pressure = 90 bar,  $50^\circ\text{C}$ ), the hydrogenation is quantitative without broadening of the narrow molecular weight distribution or other detectable side reactions.

Attempts to use heterogeneous catalyst systems based on palladium in different solvents at hydrogen pressures of 90bar gave no quantitative hydrogenation of P(S-b-B-b-MMA) block copolymers. Best results were obtained with  $\text{Pd/CaCO}_3$  and  $\text{Pd}/\gamma\text{Al}_2\text{O}_3$  in THF at  $50\text{--}70^\circ\text{C}$  (2 Mol% catalyst metal relative to double bonds). In this case 85 Mol% of the double bonds were hydrogenated without side reactions.

#### Acknowledgments

This work has been supported by the BMFT and BASF through joint project number 03M 40414 and by the German Science Foundation through Sonderforschungsbereich SFB 262 - Glaszustand und Glasübergang nichtmetallischer amorpher Materialien.

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Accepted January 10, 1993 C



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